5-19-1951

Sulphidizing of Cerussite

Emil A. Kovacevich

SULPHIDIZING OF CERUSSITE

A Thesis
Submitted to
the Department of Mineral Dressing
Montana School of Mines

In Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science in Metallurgical Engineering
(Mineral Dressing Option)

By
Emil A. Kovacevich
May 19, 1951

SULPHIDIZING OF CERUSSITE

A Thesis
Submitted to
the Department of Mineral Dressing
Montana School of Mines

In Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science in Metallurgical Engineering
(Mineral Dressing Option)

By
Emil A. Kovacevich
May 19, 1951

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLES

FIGURES

INTRODUCTION

The oxide minerals, such as cerussite, are not as amenable to flotation as the sulphide minerals. Sulphidization is the usual means used today to increase the recovery of an oxide flotation; however, sulphidization under the most advantageous conditions does not yield very satisfactory recoveries. It is, of course, a useful adjunct to the usual flotation methods and its use will aid in minimizing the loss of the oxide minerals. Contrasting the effectiveness of copper sulphate for the activation and subsequent flotation of sphaterite, the ineffectiveness of sulphidizing is very noticeable. Consequently, this investigation is the continuation of a study carried on in the Mineral Dressing Laboratory in the Montana School of Mines to interpret and determine the reason for the ineffectiveness of sulphidization.

Sulphidizing can be accomplished by the use of various methods and reagents. The ways used are (1) by the use of hydrogen sulphide on either the dry or the wet crushed ore, (2) by the use of solutions of the various sulphides and sulpho-compounds of sodium, (3) by the use of solutions of the various sulphides and sulpho-compounds of calcium, (4) by the use of sulphur vapor, (5) by the use of sulphureted oil, (6) by the use of colloidal sulphur. The use of Na_2S as a sulphidizing reagent has been widely accepted commercially, because it is economical, easier to manufacture, available and more effective.

LITERATURE REVIEW

Sulphidizing was regarded as the process involving the coating of oxidized minerals with a monomolecular film of an insoluble compound, e. g., lead sulphide.

A patent[2] was applied for and received on December 19, 1905, by Alfred Schwarz on the "Process of Concentrating Ores", which was the first patent on sulphidization.

The theory for sulphide filming of the lead carbonate has been adopted by Varley[3]. According to his theory, sodium sulphide hydrolized according to the following equations:

(1) $Na_2S + H_2O \longrightarrow NaOH + NaHS$.

$PbCO_3$ is soluble in NaOH as follows:

(2) $PbCO_3 + 3NaOH \longrightarrow NaHPbO_2 + H_2O$.

(3) $NaHPbO_2 + NaHS \longrightarrow PbS + 2NaOH$.

Combining Numbers 1, 2, and 3, we have:

(4) $Na_2S + PbCO_3 \longrightarrow PbS + Na_2CO_3$

The PbS formed is insoluble in dilute acids or alkalies.

Varley's summary of sulphidization is based on chemical reaction, and this reaction need not be essentially one that is confined only to the surface. Thus, the reaction need not proceed further than a surface film for sulphidizing in a flotation operation. Under such conditions, the metathetical reaction necessary for conditioning the lead carbonate mineral surface would be a type of exchange adsorption[4] between the lattice ions on the surface and the ion in solution.

The exchange adsorption would be of the type as shown by Kolthoff and is expressed as:

$$PbCO_3 + S^{=} \text{ -- } PbS + CO_3^{=}$$

This exchange would be in the ratio of one sulphur for one carbonate ion.

According to Wark[5] the surface of the lead sulphate will be changed to lead sulphide since lead sulphide is less soluble than lead sulphate. This is indicated by the equation:

$$PbSO_4 + S^{=} \text{ -- } PbS + SO_4^{=}$$

Wark states that the blackening of the white anglesite mineral indicates that the reaction occurs to considerable depth. He is apparently implying a penetration of the reaction into the mineral rather than just a surface condition.

With the depletion of higher-grade sulphide deposits, the recovery and benificiation of oxide minerals is assuming a more important status. Already a procedure for treating local oxide copper ores has been adopted.

Cerussite[6] is a fairly common mineral and it occurs in conjunction with other lead minerals. It occurs in simple tabular prismatic, or pyramidal rhombic or pseudo-hexagonal crystals; and in groups or aggregates of crystals; it rarely occurs fibrous, but it often is granular, massive, or compact, and, maybe, earthy. The color may be white or may be more or less tinged grey. The solubility of lead carbonate ranges from 1.0×10^{-13} to 1.5×10^{-13}. The specific gravity[7] of cerussite is 6.55 (high for a mineral with nonmetallic luster). Hardness ranges from 3 to $3\frac{1}{2}$

with prismatic (110) cleavage. It is transparent to sub-translucent.

The conclusions from sulphidized flotation tests made by W. D. Finnegan[1] were as follows:

1. The common frothers do not give a stable froth.
2. The addition of sodium sulphide raises the pH of the circuit, but the variation may be erratic.
3. Desliming the ore prior to flotation increased the grade and recovery and decreased the consumption of reagents.
4. Heavy media separation of the sands showed little concentration.
5. Better results were achieved if sulphidizing is carried out in a thick pulp.
6. The sodium sulphide is advantageously added continously or in stages to the flotation cell.

In the stabilization of the pH in his tests, sodium sulphide was buffered with boric acid. (Acetic or boric acid may be used.) It was also observed that the sulphide coating during flotation disappeared. This was possibly attributed to abrasion by agitation of the pulp.

CONTACT ANGLE STUDIES

Contact Angle. Contact angles[8] are a measure of the adhesion between bubbles and particles. (Contact angles are not limited to systems in which all the phases are fluid.)

The relations[9] between the two fluid phases and the solid phase can be viewed with respect to the tendency exhibited by a gas to displace water from contact with a mineral surface. The contact angle is measured in the liquid phase and occurs as the angle between the mineral or solid phase and the gas or air phase. The angle can be measured on a photograph of a bubble in contact with a mineral. For a complete discussion of contact angle the writer refers to Wark[5] and to Gaudin[10].

Contact Angle Apparatus. The contact angle apparatus used in this study was similar to Finnegan's[1] and to that of Baarson's [11].

A 35 mm Leica camera, Model IIIC, with a micro-attachment, was used for photographing the contact angle. The camera has a side tube provided for veiwing the bubble. The camera attachment was connected to a Bausch and Lomb microscope that focused and magnified the bubble. A rectangular glass cell was used to hold the solution and the sample was held suspended in this by a mount-holder and a height-regulator. Two microscope body-tubes were used for controlling the size and pressure of the bubble. The lower tube adjusted the distance of the bubble tube with respect to the mineral surface, and the upper tube controlled the pressure of the system. A 100 watt mercury-arc lamp was employed as a light source. The apparatus employed is the same as that used by Finnegan[1] except the apparatus was mounted different. The camera, glass cell holder and the mercury-arc lamp moved on a ramp, which was bolted to the laboratory desktop.

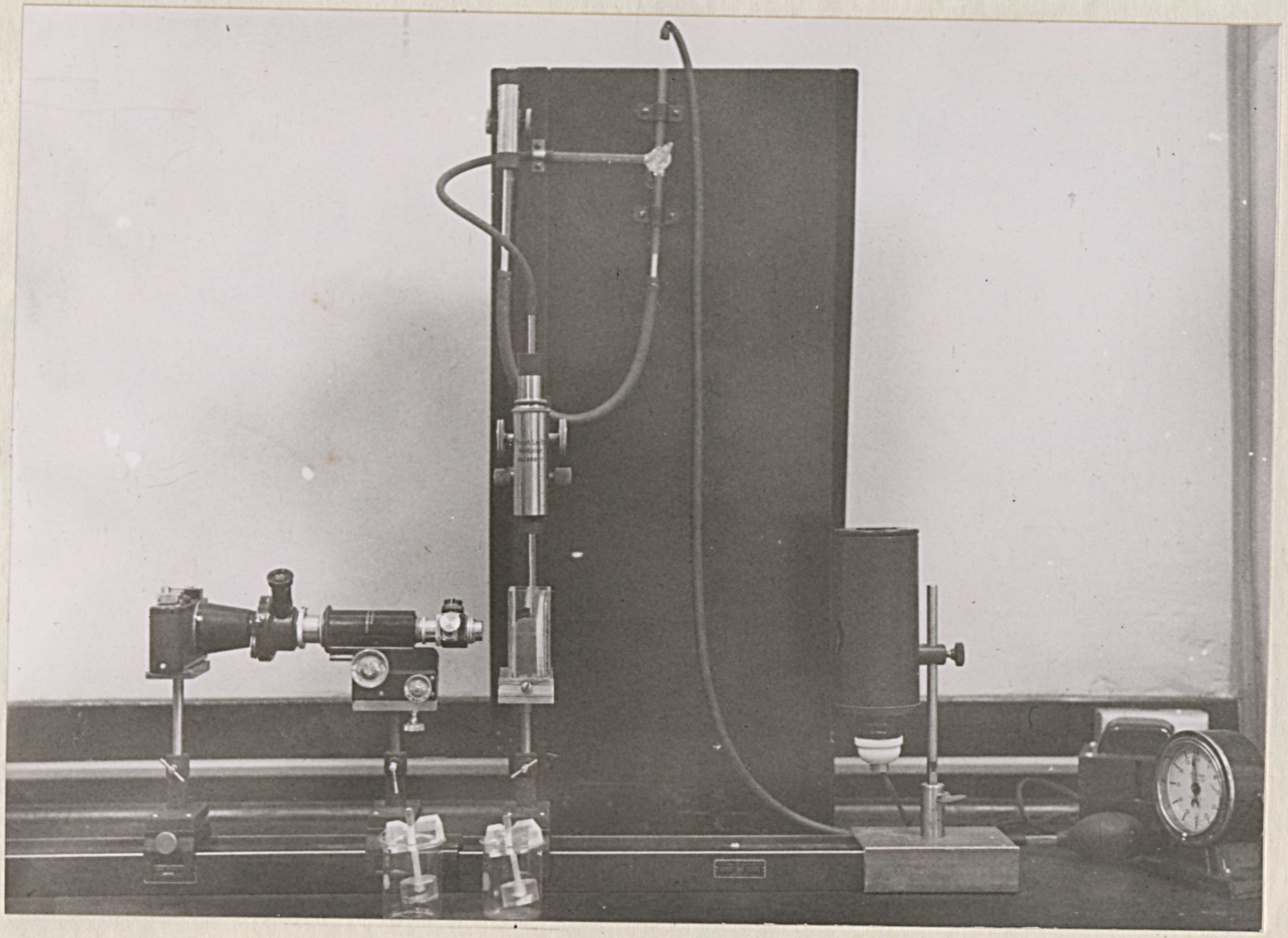

Figure 1. Contact Angle Apparatus

This gave a more stable system. The bubble tube apparatus was also secured by means of two angle braces.

Panatomic-X film and suitable developing solutions were used.

A Beckman pH meter was used in determining the pH of the various solutions. Calomel and glass electrodes were used in the pH meter.

An electrical agitator was used to stir the Na_2S solution while sulphidizing.

Preparation of Minerals. The samples of cerussite used in the contact angle studies were supplied by Dr. E. S. Perry, Professor of Geology at the Montana School of Mines. These samples were obtained from a large crystal of cerussite, and were exceptionally pure and compact.

The cerussite samples were mounted in lucite, and the mounting drilled and threaded to fit a threaded rod which held and positioned the mounting in the contact cell.

Preparation of Solutions. A stock solution of Na_2S solution containing a Na_2S concentration of 8 grams per liter of distilled water was made. There was no adjustment for pH made here at this point. Using a 250 ml volumetric flask and a 50 ml burette, subsequent dilutions to the desired Na_2S concentrations were obtained. The pH of these different solutions were taken and recorded. Table 1 gives the dilutions and their respective pH. After the preparation of the desired concentration of Na_2S solutions, the pH was adjusted to 8.5 with either 0.1 N NaOH or 0.1 N HCL.

Conc. of Na_2S (mg/l)	ml of Na_2S (8 g/l)	ml of water	pH
8000	250.00	0.00	12.25
6000	187.50	62.50	12.12
4000	125.00	125.00	12.00
2000	62.50	187.50	11.75
1000	31.25	218.75	11.41
500	15.63	234.37	11.15
250	7.81	242.19	10.82
125	3.91	246.09	10.37
62.50	1.95	248.05	9.75
31.25	0.93	249.07	8.15
15.63	0.47	249.53	7.10
7.81	0.23	249.77	6.90
0.00	0.00	250.00	6.20

Table I--Table of Dilutions

A 25 mg/liter solution of potassium ethylxanthate was prepared and the pH of the solution was adjusted to 8.5.

Mineral Testing. The mounted specimen was polished on a polishing lap using stannic oxide as the abrasive. A micro-cloth was found to give satisfactory polishing results. During the lap polishing a steady stream of distilled water was employed. After polishing and thoroughly washing the specimen, the sample was immediately transferred to a beaker containing distilled water to prevent the mineral surface to come in contact with the air or to become dry. The sample was then transferred to the contact angle cell.

The 'cleanliness' test was then made. Cleanliness in the usual sense as applied to contact angle studies is not entirely appropiate in this investigation. Usually, cleanliness indicates no contact on such minerals as untreated galena, sphalerite, etc.. However, cerussite[6] exhibits in a water solution a very considerable solubility, e.g., cerussite has a solubility range of 1.0×10^{-13} to 1.5×10^{-13}. Thus, the surfaces of cerussite is continually undergoing a change through a reaction with the water phase and the result being that a zero contact angle was not achieved.

Sulphidizing. After the 'cleanliness' test having been completed, the mounted specimen was placed in the sulphidizing solution of pre-determined strength for a period of one minute. At the elapse of this time period, the specimen is withdrawn and thoroughly washed in distilled water.

The specimen was then transferred to the contact angle cell, which contains the xanthate solutions.

Contact. As soon as it was manipulatively possible, a bubble was placed at the surface of the specimen. The stop watch was immediately started upon placing the sulphidized specimen in the contact angle cell. (A period for reaction may be necessary.) At the time equilibrium was achieved, a photograph was taken whether or not a contact angle was formed with the specimen. From the equilibrium phase, photographs were taken in 5 minute intervals up to 20 minutes. For each time interval (5, 10, 15, and 20 minute interval) a new bubble was placed on the mineral surface area.

Several methods were employed to assure that the bubble was in equilibrium. Tapping of the cell helped somewhat, but it had to be done very gently or the bubble would spread or be lost completely. Baarson's[11] more accurate methods of attaining equilibrium are the circular highlight method and the test wherein slight changes in pressure achieve gentle back and forth vibrations. These latter two tests, coupled with the operator's visual observation of a bubble in near equilibrium, enabled satisfactory pictures to be taken.

The pH of the xanthate solution before conducting the test and after the test were taken and recorded. The temperature of each test solution was also noted.

Skewing of the bubble was coped with and was extremely bothersome in the operations. One chief cause for the skewing was noticed during the operation. The specimen mount-holder did not fit flush on the sides on the cell walls and the threads for the rod holding the specimen had enough play so the least movement would move the mineral surface. With experience and patience of the operator, this barrier can be overcome.

Measurements. The film containing the photographed bubbles was processed and projected by the use of an Omega enlarger on a white screen. The contact angles were measured five times on the right and lift sides and the average for each side recorded. The film is filed in a book that is kept in the Mineral Dressing Department in the Montana School of Mines.

SUMMARY

Solubility of Cerussite. As it was discussed previously, it was practically impossible to get zero contact angle in the initial concentration of 0.0 mg of Na_2S in one liter of distilled water. In Finnegan's[1] work a contact of 30.7° was obtained and in the author's work a contact angle of 30.2° was observed. This is definitely attributed to the solubility of the cerussite in water. The solubility of the mineral surface changes the surface energy, thus, changes the adsorptive property of the mineral.

Cerussite[12] has a solubility product of 3.3×10^{-14} at 18°C. Contrasting to this solubility, the solubility product of copper sulphide and lead sulphide are 8.5×10^{-45} and 3.4×10^{-28} respectively at 18°C.

Solubility of cerussite[12] in 100 ml of cold water is 0.00011 grams at 20°C. Cuprite (Cu_2O), tenorite (CuO), Cassiterite (SnO_2), and rutile (TiO_2), are all insoluble in cold or hot water. Zincite (ZnO) will dissolve (0.00016 grams) in 100 ml of water at 29°C.

Replacement by Sulphur Ion. At low concentration, the sulphur ions from the solution may, by exchange adsorption[4], replace the carbonate ions in the lattice of the cerussite. The sulphur ion[13] has an atomic radius of 1.84 A°. This approximates the radii of the carbonate ion in the lattice of the cerussite in 2 directions, but is 0.44 A° less than the sulphur ion in the third direction. It may be assumed that any exchange between the sulphur and carbonate ions to depths greater than one molecule will exert forces that tend to distort the original crystal lattice configuration at or near the surface. If the sulphur ion fits precisely into the site of the carbonate ion, the reaction would stop since the two products necessary for the reaction would be separated by the insoluble film of PbS; thus, a monomolecular film would possible form.

Capillary Action. Since it has been conceived that the sulphur ion does not fit exactly in the carbonate ion site, there is a possibility of solution penetration of the cerussite crystal lattice by capillary action. This penetration

could be the explanation for the presence of a black scum or film during a flotation of sulphidized oxide lead minerals which was encountered by Finnegan[1] and others. The disintegration of the compact cerussite lattice would emit particles of PbS into the solution and form a layer on top of the solution in the cell. This was analyzed and it was definitely found to contain Pb.

During flotation of sulphidized minerals in a commercial operation, the mill operator used the presence of this black PbS scum as a guide to prevent over-sulphidization.

Possible Reactions. A group of reactions[#] have been developed to support the author's theory of sulphidization. These are different from those presented early by Varley[3]. The reactions are as follows:

$$Na_2S + H_2O \longrightarrow NaOH + NaHS$$

$$Na_2S + 2H_2O \longrightarrow 2NaOH + H_2S \uparrow$$

$$PbCO_3 + 2H_2O \longrightarrow Pb(OH)_2 + H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2 \uparrow$$

$$Pb(OH)_2 \rightleftharpoons H_2PbO_2$$

$$2NaOH + H_2PbO_2 \longrightarrow Na_2PbO_2 + 2H_2O$$

$$NaOH + H_2PbO_2 \longrightarrow NaHPbO_2 + H_2O$$

$$PbCO_3 + Na_2S \longrightarrow PbS + Na_2CO_3$$

$$NaHPbO_2 + H_2S \longrightarrow PbS + NaOH + H_2O$$

$$PbS + NaOH \text{ (excess)} \longrightarrow Na_2PbO_2 + H_2S$$

Dr. E.G. Koch and Dr. K.N. McLeod, Department of Chemistry, Montana School of Mines, and Professor D.W. McGlashan, Department of Mineral Dressing, Montana School of Mines.

CONCLUSIONS

The solubility of cerussite in a water solution definitely contributes to the paritial effectiveness of sulphidizing. Additionally, its solubility prevents application of the usual contact angle procedure in the 'cleanliness' testing, that is, impossibility in obtaining a zero contact angle. Consequently, these factors must be kept in mind in order that discussion of the experimental evidence obtained in this investigation may be readily understood.

The film is not just monomolecular, but a multilayer film. This can be readily seen by a sulphidizing test on several samples of cerussite. In a strong sodium sulphide solution, the sample is blackened quickly, which indicates the reaction is rapid. The color is indicative of the thickness.

The addition of sodium sulphide to a solution usually varies the pH of that solution (usually increases the pH). This was observed when the sodium sulphide solution was prepared. The initial pH of the liter of distilled water was 6.2 and the final pH after the addition of eight grams of sodium sulphide was 12.25. This would indicate that in high concentrations sodium sulphide would act as a depressant for the oxide minerals due to the increase of the hydroxyl ion concentration. Rogers and Sutherland states[14], "All minerals adsorb hydrogen ions or hydroxyl ions so that the pH value of

the solution will largely determine the adsorptive properties of the mineral."

It is shown in the data herein, (Figure 2) that there is similarity between the author's work and previous work conducted by W. D. Finnegan. It must be remembered, however, that due to the large amount of variable factors involved in such an investigation as this, it is impossible to repeat the data exactly. Such contributing factors as the degree of polishing on the specimen, compactness of the specimen, crystal orientation, etc. will vary with each test and in different samples.

As the concentration of the sulphidizer was increased, the contact angle increased to a maximum, and then decreased. The film may have contained a lead compound (perhaps lead sulphide) at various thicknesses, but as indicated by the previously presented chemical reactions, in all probability, there were other compounds present in the film at the same time.

Changes in composition of the film at various thicknesses appear likely, and it is also believed that the orientation of the complexes varied. The decrease in contact angle between 500 and 1000 milligrams per liter may be accounted for by a change in the orientation formed.

At certain orientations and thicknesses the surface presented spots and areas at which the xanthate ion was adsorbed.

In Figure 3, it can be seen that between the range of

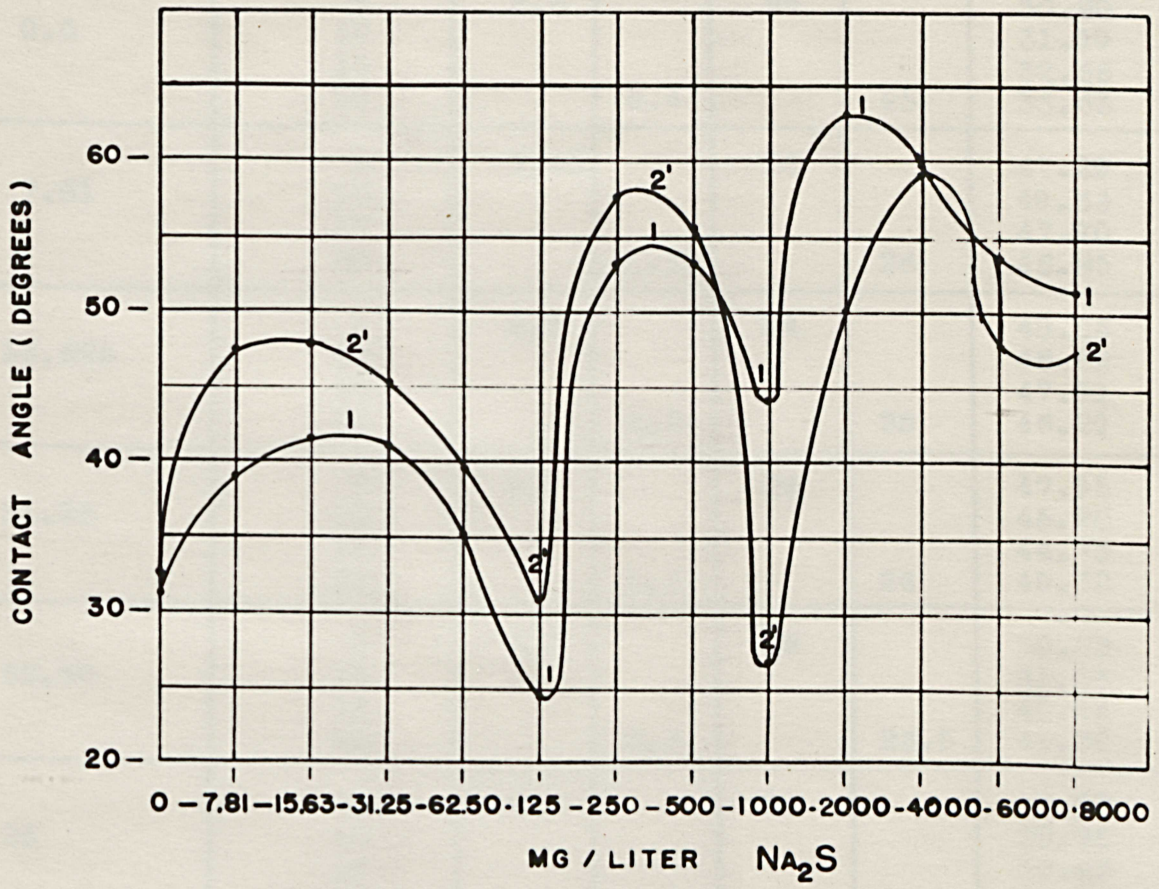

FIGURE 2 – CONTACT ANGLE MEASUREMENTS ON CERUSSITE WITH VARIATION IN CONCENTRATION OF SODIUM SULPHIDE (25 MG / LITER POTASSIUM ETHYL XANTHATE). pH – 8.5.

1. FINNEGAN, W.D., OP. CIT., P.33.

2'. AUTHOR'S DATA (SEE TABLE II).

Conc. of Na_2S solution mg/liter 8.5 pH	Stability Time, Min.	pH		Temp. (°C)		Contact Angle in Degrees
		Start	End	Start	End	
0.0	5	8.6		24		30.20
	10					31.99
	15					32.66
	20		8.4		25	33.63
7.81	5	8.45		24		47.29
	10					49.63
	15					47.90
	20		8.10		26	48.85
15.625	5	8.6		24		48.06
	10					48.82
	15					47.91
	20		8.2		25	46.29
31.25	5	8.5		24		47.95
	10					45.20
	15					44.75
	20		8.3		26	45.32
62.50	5	8.7		25		35.23
	10					31.35
	15					40.24
	20		8.3		26.5	41.50
125	5	8.7		24		36.27
	10					25.25
	15					30.85
	20		8.2		26	44.26
250	5	8.7		24		53.50
	10					55.25
	15					58.12
	20		8.7		25.5	59.23
500	5	8.6		24.5		57.26
	10					58.10
	15					55.42
	20		8.2		25	57.23
1000	5	8.7		25		23.02
	10					24.56
	15					26.12
	20		8.5		26	24.14

Table II--Contact Angle Measurements on Cerussite with Variation in Concentration of Sodium Sulphide (by the author). Continued on next page.

Conc. of Na_2S solution mg/liter 8.5 pH	Stability Time, Min.	pH		Temp. (^oC)		Contact Angle in Degrees
		Start	End	Start	End	
2000	5	8.6		24		43.45
	10					48.52
	15					50.25
	20		8.4		26.5	49.63
4000	5	8.5		25		61.36
	10					63.42
	15					59.27
	20		8.5		26.5	64.04
6000	5	8.6		24.5		53.50
	10					54.52
	15					47.75
	20		8.4		25.5	54.73
8000	5	8.7		24		48.50
	10					48.97
	15					47.23
	20		8.6		25.5	44.42

Table II--Contact Angle Measurements on Cerussite with Variation in Concentration of Sodium Sulphide (by the author). Continued from preceding page.

Na_2S solution mg./liter	Stability Time, Min.	pH		Temp. °C	Contact Angle in Degrees
		Start	End		
0.0	10 15 20	8.9	8.9	26	38.2 30.7 41.4
7.85	10 15 20	8.3	8.0	26	41.6 41.3 38.4
15.7	10 15 20	8.1	7.5	24	43.3 41.6 36.5
31.4	10 15 20	8.9	8.7	25	41.4 42.2 42.0
62.8	10 15 20	8.8	8.8	26	34.3 35.4 36.8
125.6	10 15 20	8.4	8.2	27	22.5 24.3 20.5
251.2	10 15 20	8.9	8.9	27	50.5 53.4 55.6
502.4	10 15 20	8.9	8.9	26	52.3 53.3 51.8
1000	10 15 20	8.9	8.9	27	39.6 44.0 45.5
2000	10 15 20	8.8	8.7	27	62.3 63.4 61.3
4000	10 15 20	8.5	8.5	27	60.4 60.2 58.9
6000	20	8.9	8.9	26	53.3
8000	10 15 20	8.6	8.5	26	51.6 53.6 54.4

Table III--Contact Angle Measurements[1] on Cerussite with Variation in Concentration of Sodium Sulphide.

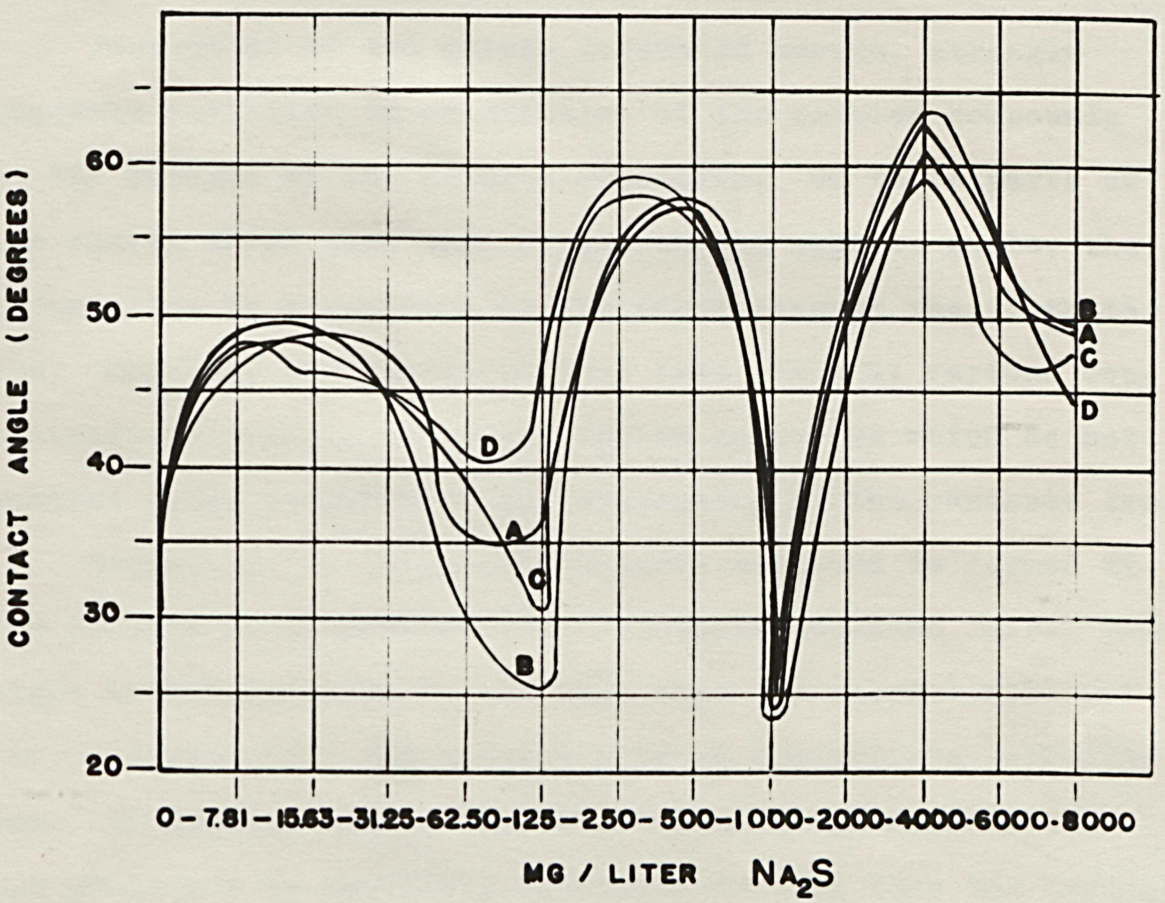

FIGURE 3 – STABLIZATION TIME CURVES (5,10,15,20 MIN.) SHOWING CONTACT ANGLE MEASUREMENTS ON CERUSSITE WITH VARIATION IN CONCENTRATION OF SODIUM SULPHIDE (25 MG / LITER POTASSIUM ETHYL XANTHATE). pH- 8.5

A. CONDITIONED FOR 5 MINUTES.
B. " " 10 MINUTES.
C. " " 15 MINUTES.
D. " " 20 MINUTES.

0 and 250 milligrams of sulphidizer that a stabilization period is needed when sulphidizing in this range. Beyond this range, the curves are fairly coherent, thus, reducing the need of a stabilizing period.

Inspection of the curves presented herein, strongly suggests variation in orientation of the complex compounds at the surface of the soluble cerussite. On those parts of the curves which show high or increasing contact angle, the orientation is acceptable to the adsorption of the xanthate ion. However, the reactions that take place at various concentrations produce oriented complex compounds which do not present sites suitable to the adsorption of the xanthate ion.

Certainly, no relatively soluble compound is formed at the surface in accordance with Paneth-Fajans-Hahn rule. This might be attributable to the fact that the sulphur will not fit precisely into the lattice site of the surface carbonate ion. It appears likely that the sodium sulphide solution can penetrate by capillary diffusion further into the crystal. This is in marked contrast to the activation of sphalerite by copper sulphate. The copper ion and the zinc ion having approximately the same atomic radii can be considered interchangeable in the lattice. Consequently, the copper ion forms copper sulphide at the surface which is relatively more insoluble than the former zinc sulphide surface.

Practically speaking, sodium sulphide for the activation of cerussite will never be positive in its action in contrast

to the effect of copper sulphate. Certainly, if all the particles of cerussite in the pulp could attain a film of proper orientation suitable for xanthate adsorption, the resulting flotation separation would be very successful. However, this is inherently impossible by the very nature of the mineral, and the reactions produced at or near the surface by the addition of sodium sulphide.

RECOMMENDATIONS

The future study of sulphidizing should consider the following proposals:

1. Initially, the sulphidizing tests were conducted at the same pH of 8.5 (both the xanthate solution and the sodium sulphide). The possible research routes should include the following pH changes:

   (a) The changes in pH made will be in the xanthate solutions. Suggests pH values of 6.5, 7, 7.5, 8, and 9.

   (b) The change in pH will be made in the sulphidizing solution while the xanthate solution's pH be held constant.

   (c) Change the pH of the sulphidizing solution and the xanthate solution to the same value other than 8.5.

2. A procedure and analysis should be developed to analyze the gas formed upon sulphidization.

3. With the use of slow X-rays, the thickness of the film could be ascertained.

4. Using radio-active elements (tracers) the exact mechanism of sulphidization may be further realized.

5. The solubility of cerussite in different size ranges should be established and checked against the known solubility.

6. Other methods of activation other than sulphidization should be studied. Mercaptans may replace the carbonate ion and thus, the adsorption of another collector would not be needed.

7. A method of positive cationic adsorption with barium or some other element which with the carbonate ion would produce an insoluble film. In this type of exchange adsorption, the barium ion would replace the lead ion to form the insoluble barium carbonate film.

BIBLIOGRAPHY

1. Finnegan, W. D.: Sulphidizing of Lead Oxide Minerals. M. S. thesis, Montana School of Mines, Butte. 1949.
2. U. S. Patent Office: Process of Concentrating Ores. Alfred Schwarz. Dec. 19, 1905.
3. Varley, T.: The Flotation of Oxidized Ores; pt. I. Mining Journal, Vol. 11, No. 14, p. 6-7, Dec. 15, 1927.
4. Koltoff, I. M.: Adsorption on Ionic Lattice. Journal of Physical Chemistry, Vol. 40, p. 1027, 1936.
5. Wark, I. W.: Principles of Flotation. Australian Institute of Mining and Metallurgy, Inc. 1938.
6. Mellor, J. W.: A Comprehensive Treatise on Inorganic and Theoretical Chemistry; Vol. VII, p. 829-830. Longmans, Green and Co. 1927.
7. Hurlbut, C. S.: Dana's Manual of Mineralogy. P. 234. John Wiley and Sons, Inc. 1946.
8. Taggert, A. F.: Handbook of Mineral Dressing; Chap. 12, p. 38. John Wiley and Sons, Inc. 1947.
9. Gaudin, A. M.: Flotation; p. 33. McGraw-Hill Book Company, Inc. 1932.
10. Gaudin, A. M.: Principles of Mineral Dressing; p. 338. McGraw-Hill Book Company, Inc. 1939.
11. Baarson, R. E.: A Study of the Effect of Potassium Ethyl Xanthate at Sulphide Mineral Surfaces with Changes in Temperature. M. S. thesis, Montana School of Mines, Butte. 1949.

12. Handbook of Chemistry and Physics, 30th ed. Chemical Rubber Publishing Co. 1947.

13. Bragg, W. L.: Atomic Structure of Minerals, Cornell University.

14. Rodgers, J. and Sutherland, K. L.: Principles of Flotation-Activation of Minerals. A. I. M. E. Technical Publication, No. 2082. 1946.

ACKNOWLEDGEMENT

The author is greatly indebted to Research Professor Donald W. McGlashan, Professor of the Department of Mineral Dressing, under whose supervision this investigation was conducted; and to Dr. Edwin G. Koch and Dr. Kenneth N. McLeod, Department of Chemistry, both who served as general consultants on this problem; and to Mr. Wilbur J. Guay for his able assistance during the progress of this investigation.